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SPECTROSCOPIC STUDIES OF THE ASSOCIATIONS OF HETEROCYCLIC AMINES

(2-Amino-methyl Pyridines and Amino-quinolines)

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Received June 5, 1961

(Communicated by Dr. R. K. Asundi, F.A.SC.)

I. INTRODUCTION

HETEROCYCLIC amines have been studied in considerable detail by ultra-violet absorption spectroscopy.[1-2] Angyal and Werner[3] and Goulden[4] recorded the infra-red spectra of amino pyridines and some amino-quinolines in the 3 μ region, but the data given by these workers are incomplete. The authors[5] have studied the associations in amino-pyridines and assigned the N–H vibrational frequencies of these substances. There appears to be no mention in literature in regard to the infra-red studies of associations in 2-amino-methyl pyridines and amino-quinolines. The authors have recorded the infra-red spectra of 2-amino methyl pyridines and amino-quinolines and in solutions at various concentrations to study:

(1) their intermolecular associations, the apparent molecular extinction coefficients of the various bands in the 3 μ region and the assignment of the N–H stretching frequencies,

(2) the shifts in the N–H in-plane deformation frequencies from solid to dilute solutions, and

(3) account for a strong absorption band in the region of 2950 cm.$^{-1}$ in case of all the compounds in solutions of chloroform.

II. EXPERIMENTAL

A Perkin-Elmer Infra-red Spectrophotometer Model 21 with NaCl optics was used to obtain the spectra. The details of experimental techniques have been described by the authors in earlier communications.[5-7]

The 2-amino-methyl pyridines were from B.D.H. and 3-amino-quinoline was of 'Light' make. 2- and 4-amino-quinolines were synthesised. All the compounds and solvents were purified by the conventional methods.

III. RESULTS

The infra-red frequencies of the amines and in solutions as recorded by the authors in the 3 μ and 6 μ regions are given in Table I, and the traces

TABLE I

N-H Stretching and deformation bands of 2-amino-methyl pyridines and amino-quinolines ($cm.^{-1}$)

Amine	Nature of the band	Bands of pure amine	Bands of the amine in carbon tetrachloride or in chloroform
2-Amino-3-methyl pyridine	N–H Stretch N–H Deform	3450, 3320, 3175, 1634	3520, 3425, 3320, 3180, 1621
2-Amino-4-methyl pyridine	N–H Stretch N–H Deform	3435, 3300, 3165, 1642	3510, 3415, 3335, 3175, 1623
2-Amino-5-methyl pyridine	N–H Stretch N–H Deform	3450, 3320, 3175, 1634	3510, 3420, 3335, 3185, 1621
2-Amino-6-methyl pyridine	N–H Stretch N–H Deform	3450, 3320, 3175, 1634	3510, 3415, 3310, 3175, 1621
2-Amino-quinoline ..	N–H Stretch N–H Deform	3450, 3310, 3175, 1642	3510, 3420, 3320, 3185, 1623
3-Amino-quinoline ..	N–H Stretch N–H Deform	3445, 3335, 3195, 1631	3485, 3400, 3340, 3220, 1621
4-Amino-quinoline ..	N–H Stretch N–H Deform	3425, 3320, 3175, 1647	3510, 3420, 3335, 3175, 1623

of the corresponding absorption bands of 2-amino 5-methyl pyridine in carbon tetrachloride and of 2-amino-quinoline in chloroform at various concentrations are given in Figs. 1 and 2. From these observations, it is seen that the pure 2-amino-methyl pyridines and amino-quinolines have three absorption bands in the 3 μ region, but in solutions of carbon tetrachloride or chloroform four distinct and well-defined bands could be recorded in the region of 3510, 3420, 3330 and 3185 $cm.^{-1}$ With the increasing dilution of amines in solutions of carbon tetracholoride or chloroform, the first two bands appear more prominently than the other two. The frequencies in the region of 3510 $cm.^{-1}$ and 3420 $cm.^{-1}$ of 2- and 4-amino-quinolines in solutions have

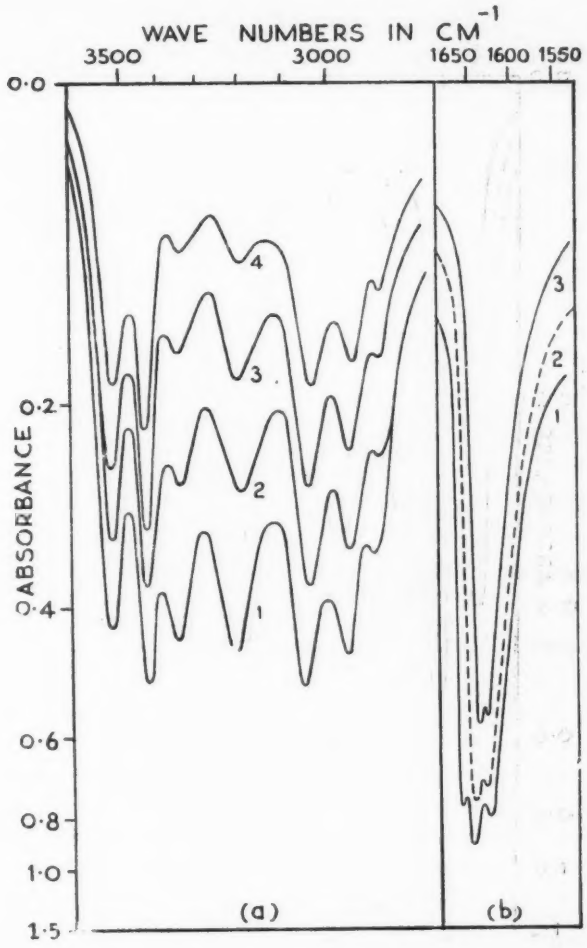


FIG. 1. (*a*) NH_2, CH and CH_3 stretching absorption bands of 2-amino-5-methyl pyridine in carbon tetrachloride. (1) 0·26 Mol. conc. (2) 0·19 Mol. conc. (3) 0·13 Mol. conc. (4) 0·088 Mol. conc. (*b*) NH_2 in-plane deformation and ring absorption bands. (1) 0·26 Mol. conc. (2) 0·13 Mol. conc. (3) 0·088 Mol. conc.

same values, but the corresponding frequencies of 3-amino quinolines have smaller values.

IV. DISCUSSION

The 2-amino-methyl pyridines and amino-quinolines may form intermolecular associations of the N–H.....N type as indicated below. The

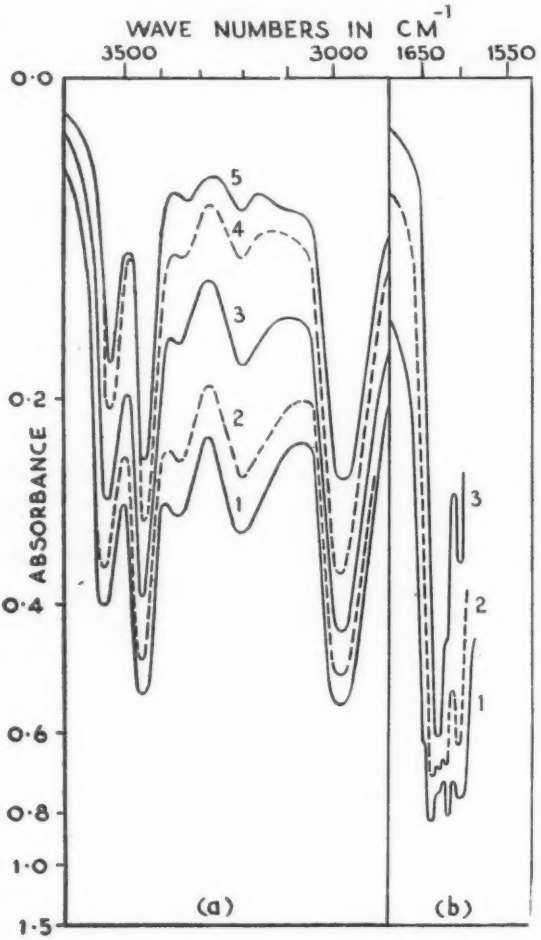
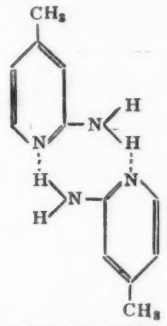


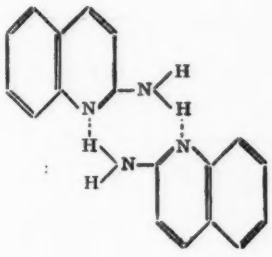
FIG. 2. (*a*) NH_2 and CH stretching absorption bands of 2-amino-quinoline in chloroform. (1) 0·42 Mol. conc. (2) 0·35 Mol. conc. (3) 0·26 Mol. conc. (4) 0·18 Mol. conc. (5) 0·12 Mol. conc. (*b*) NH_2 in-plane deformation and ring absorption bands. (1) 0·26 Mol. conc. (2) 0·12 Mol. conc. (3) 0·06 Mol. conc.

infra-red absorption spectra of these substances in solutions may therefore contain bands characteristic of bonded and free N–H vibrations. If $\epsilon_{max.}(m)$ and $\epsilon_{max.}(d)$ are the apparent molecular extinction coefficients of the absorption bands arising out of the same mode of vibration of monomers and dimers in solution at molar concentration 'c' the ratio $c\epsilon^2_{max.}(m)/\epsilon_{max.}(d)$ is

constant. The authors have used this expression in their studies of amides[6] and amino-pyridines.[5]



2-amino-4-methyl pyridine dimer



2-amino-quinoline dimer

The apparent molecular extinction coefficients of the absorption bands in the region of 3510, 3420, 3330 and 3185 cm.$^{-1}$ of each compound have been calculated at different concentrations in solutions of either carbon tetrachloride or chloroform depending upon their solubility. In case of each compound, the values of $c\epsilon^2_{max.}(a)/\epsilon_{max.}(d_1)$ and $c\epsilon^2_{max.}(s)/\epsilon_{max.}(d_2)$ have been calculated at different concentrations and these observations are given in Tables II and III. In these ratios, $\epsilon_{max.}(a)$ $\epsilon_{max.}(s)$, $\epsilon_{max}(d_1)$ and $\epsilon_{max.}(d_2)$ are the apparent molecular extinction coefficients of the absorption bands in the region of 3510, 3420, 3330 and 3185 cm.$^{-1}$ respectively. These ratios are constant to about 8 per cent. The constancy of the ratio $c\epsilon^2_{max.}(a)/\epsilon_{max.}(d_1)$ indicates that if the band in the region of 3510 cm.$^{-1}$ in each compound is due to N–H asymmetric stretching vibrations of the monomers then the one in the region of 3330 cm.$^{-1}$ is due to the same mode of vibrations of the dimer. Similar constancy of $c\epsilon^2_{max.}(s)/\epsilon_{max.}(d_2)$, in case of bands in the region of 3420 and 3185 cm.$^{-1}$ of each amine, is a consequence of the fact that they are due to N–H symmetric stretching vibrations of monomers and the associated molecules. The pattern of behaviour of these ratios is similar to those in amino-pyridines.[5] These assignments are deviations from those of Bellamy *et al.*,[8] who have assigned the band in the region of 3400 cm.$^{-1}$ of heterocyclic amines as due to the composite symmetric and asymmetric stretching absorptions from the bonded and unbonded N–H linkages.

Bellamy *et al.*[8] have shown that the N–H stretching frequencies of aromatic primary amines are governed by the empirical relation $\nu_s = 345{\cdot}5 + 0{\cdot}875\ \nu_{as}$, where ν_{as} and ν_s are the asymmetric and symmetric stretching frequencies. The authors have used the N–H asymmetric frequencies of

TABLE II

The apparent molecular extinction coefficients of N-H stretching absorption bands of 2-amino methyl pyridines in various solvents

Amine	Solvent	Mol. conc.	Free N-H bands		Bonded N-H bands		$\frac{\epsilon^2_{max.}(a)}{\epsilon_{max.}(d_1)}$	$\frac{\epsilon^2_{max.}(s)}{\epsilon_{max.}(d_2)}$
			$\epsilon_{max.}(a)$	$\epsilon_{max.}(s)$	$\epsilon_{max.}(d_1)$	$\epsilon_{max.}(d_2)$		
2-Amino-3-methyl pyridine	Carbon tetrachloride	0·23	18	22	18	20	4·1	5·6
		0·12	22	27	15	16	3·9	5·5
		0·068	23	31	9·4	12	3·8	5·5
2-Amino-4-methyl pyridine	Chloroform	0·34	15	18	11	11	7·0	10·0
		0·17	19	24	9·4	9·4	6·5	10·4
		0·10	23	30	7·5	8·0	7·1	11·2
2-Amino-5-methyl pyridine	Carbon tetrachloride	0·26	17	20	18	19	4·2	5·5
		0·19	18	21	15	15	4·1	5·6
		0·13	20	25	13	15	4·0	5·4
		0·088	22	27	11	12	3·9	5·2
2-Amino-6-methyl pyridine	Carbon tetrachloride	0·23	18	21	17	20	4·4	5·1
		0·14	22	26	14	17	4·8	5·6
		0·074	24	32	10	14	4·3	5·4

the monomers and the associated molecules in this relation and calculated the corresponding frequencies of N–H symmetric stretch. The calculated and the recorded values are given in Table IV. It is seen form these observations that this empirical relation is obeyed in case of the N–H stretching frequencies of monomers, the deviations of the calculated values from those of the recorded ones being only 4 cm.$^{-1}$ But this relation does not hold good in case of N–H stretching frequencies of the associated molecules. This negative result is also in agreement with the conclusions of Bellamy *et al.* who proposed that the empirical relation breaks down in cases where only one of the links is bonded.

Absorption Band in the Region of 2950 *cm.*$^{-1}$—The infra-red spectra of 2-amino-methyl pyridines and amino-quinolines have an absorption peak in the region of 3040 cm.$^{-1}$ which is assigned to C–H stretch. But in solutions of chloroform of all these compounds, a strong absorption band appears

TABLE III

Apparent molecular extinction coefficients of N-H stretching absorption bands of amino-quinolines in chloroform

Amine	Mol. conc.	Free N–H bands		Bonded N–H bands		$c\epsilon^2_{max.}(a)$	$c\epsilon^2_{max.}(s)$
		$\epsilon_{max.}(a)$	$\epsilon_{max.}(s)$	$\epsilon_{max.}(d_1)$	$\epsilon_{max.}(d_2)$	$\epsilon_{max.}(d_1)$	$\epsilon_{max.}(d_2)$
2-Amino-quinoline	0·42	10	13	7·6	8·1	5·5	9·0
	0·35	11	15	7·3	7·9	5·8	10·0
	0·26	12	16	6·5	7·0	5·8	9·5
	0·18	13	18	5·3	5·9	5·7	9·9
	0·12	15	22	5·3	6·2	5·1	9·4
3-Amino-quinoline	0·35	15	19	13	12	6·1	10·5
	0·17	19	27	10	10	6·1	12·4
	0·13	20	29	9	9·8	5·8	11·1
	0·084	21	32	6·3	7·6	5·9	11·3
4-Amino-quinoline	0·14	22	33	14	17	4·8	9·0
	0·098	25	39	13	16	4·7	9·3
	0·074	27	45	13	16	4·2	9·4
	0·050	31	49	11	13	4·4	9·3

TABLE IV

Observed and calculated frequencies of M-H stretching vibrations of 2-amino-methyl pyridines and amino-quinolines

Amine	Free N–H bands			Bonded N–H bands		
	Observed		Calculated	Observed		Calculated
	ν_{as}	ν_s	ν_s	ν_{as}	ν_s	ν_s
2-Amino-3-methyl pyridine	3520	3425	3426	3320	3180	3251
2-Amino-4-methyl pyridine	3510	3415	3417	3335	3175	3263
2-Amino-5-methyl pyridine	3510	3420	3417	3335	3185	3263
2-Amino-6-methyl pyridine	3510	3415	3417	3310	3175	3243
2-Amino-quinoline	3510	3420	3417	3320	3185	3251
3-Amino-quinoline ..	3485	3400	3395	3340	3220	3268
4-Amino-quinoline ..	3510	3420	3417	3335	3175	3263

in the region of 2950 cm.$^{-1}$ which is not present either in the spectra of pure amines or of them in solutions of carbon tetrachloride. The authors have calculated the $\epsilon_{max.}$ of this band at different concentrations and these observations are given in Table V. It is seen from these observations that the $\epsilon_{max.}$ of this band increases with the increasing dilution of the amines in chloroform.

TABLE V

The apparent molecular extinction coefficients of the absorption band in the region of 2950 cm.$^{-1}$ *of the* 2-*amino*-4-*methyl pyridine and amino-quinolines in chloroform*

Amine	Frequency	Mol. Conc.	$\epsilon_{max.}$
2-Amino-4-methyl pyridine ..	2940	0·45	16
		0·34	20
		0·17	29
		0·10	36
2-Amino-quinoline ..	2950	0·42	14
		0·35	16
		0·26	17
		0·18	22
		0·12	24
3-Amino-quinoline ..	2965	0·35	18
		0·17	27
		0·13	30
		0·084	34
4-Amino-quinoline ..	2940	0·14	39
		0·10	45
		0·074	49
		0·050	51

In solutions of chloroform, both monomers and dimers are present. The authors propose that the appearance of the band in the region of 2950 cm.$^{-1}$ is due to hydrogen bond formation between the N-atom of the monomer amines and the H–atom of the molecules of chloroform. A consequence of this bond formation is that the C–H bond of some molecules of chloroform in the sample beam is in bonded condition while the same bond in case of all the molecules of chloroform in the reference beam is a free linkage because of the absence of the solute. The bonded C–H linkage of chloroform in the sample beam is not thus compensated for with the result that the absorption band corresponding to the bonded C–H stretch in chloroform

appears in the region of 2950 cm.$^{-1}$ The small values of $\epsilon_{max.}$ of this band in solutions of 0·3 to 0·4 molar is due to the presence of smaller percentage of monomers at these concentrations. But with increasing dilution of the amines in chloroform, the intermolecular associations break up progressively and the hydrogen atoms of more chloroform molecules get opportunity to form the hydrogen-bond with the free N-atom of the increasing number of monomers. The $\epsilon_{max.}$ of the absorption band corresponding to the bonded C–H linkage of chloroform thus increases with the increasing dilution of the amine.

N–H In-plane Deformation Band.—The solid-solution shifts of N–H in-plane deformation bands have been recorded at various concentrations and the frequencies of the pure amines and in very dilute solutions are given in Table I. Solid 2-amino quinoline has a strong absorption band at 1642 cm.$^{-1}$, but at a molar concentration of 0·26 in chloroform, it is a strong band at 1634 cm.$^{-1}$ with a weak shoulder at 1623 cm.$^{-1}$ At 0·12 molar, two distinct peaks could be recorded at 1634 and 1623 cm.$^{-1}$ and finally at a molar concentration of 0·06, the band at 1634 cm.$^{-1}$ disappears completely and the one at 1623 cm.$^{-1}$ appears as a strong band. The solid 3-amino-quinoline has an absorption band at 1631 cm.$^{-1}$ and at a molar concentration of 0·35 in chloroform, the absorption has the same frequency as that of the solid, together with a weak shoulder at 1621 cm.$^{-1}$ With increasing dilution, the peak at 1621 cm.$^{-1}$ becomes more prominent and at a molar concentration of 0·044 in chloroform, only a single strong band at 1621 cm.$^{-1}$ could be recorded. The solid 4-amino-quinoline has a strong absorption band at 1647 cm.$^{-1}$ and in solutions of chloroform at a molar concentration of 0·15, the band at 1647 cm.$^{-1}$ becomes weak and an additional band appears at 1637 cm.$^{-1}$ With the increasing dilution, the band at 1647 cm.$^{-1}$ disappears completely and the peak at 1637 cm.$^{-1}$ shifts to 1623 cm.$^{-1}$ At 0·03 molar in chloroform only the strong band at 1623 cm.$^{-1}$ could be recorded. Similar shifts of this band of 2-amino-methyl pyridines have been observed from solid to dilute solutions and these observations are also given in Table I. The shift of this band towards lower frequency in dilute solutions is consistent with the assignment of this band to N–H in-plane deformation. The band at higher frequency, in each case, is due to N–H in-plane deformation of associated molecules and the one at lower frequency is due to the same mode of vibration of the monomers.

The relatively large shifts of the order of 19–24 cm.$^{-1}$ of N–H in-plane deformation in 2- and 4-amino-quinolines, compared to a shift of 10 cm.$^{-1}$ in 3-amino-quinoline may be due to the weaker intermolecular association

in the latter. This is substantiated by the fact that the difference in the N–H asymmetric and symmetric stretching frequencies of monomers and associated molecules are of the order of 180 and 240 cm.$^{-1}$ respectively in 2- and 4-amino-quinolines while these shifts are 145 and 180 cm.$^{-1}$ in 3-amino-quinoline.

This conclusion receives additional experimental evidence by the fact that the frequency of the bonded C–H stretching vibration of chloroform in the presence of 2- and 4-amino-quinolines has a smaller value than that of the corresponding band in the presence of 3-amino-quinoline.

The earlier workers[1, 2] by their ultra-violet absorption studies of heterocyclic amines, arrived at opposing conclusions about the possible existence of the molecules of these compounds in amino or imino forms, when the amino group is in 2- and 4-positions. Reisuka Soda[9] by measuring the intensities of the bands in the 3 μ region concluded that 2-amino pyridine exists predominantly in amino form. The authors[5] have assigned the N–H vibrational frequencies of amino-pyridines on the basis of the presence of NH_2 group in these molecules. The presence of four absorption bands in the region of 3510–3175 cm.$^{-1}$ in the 2-amino-methyl pyridines and amino-quinolines, the variation of their $\epsilon_{max.}$ with increasing dilution and the constancy of $c\epsilon^2_{max.}(m)/\epsilon_{max.}(d)$ in case of these absorption bands give a quantitative evidence for the presence of intermolecular associations and primary amino group in these compounds. The presence of strong N–H in-plane deformation band in the spectra of pure substances and its shift towards lower frequency in dilute solutions give additional evidence. The experimental evidence, thus, does not indicate for the existence of imino forms in these compounds even when the amino group is in 2- or 4-positions.

V. SUMMARY

The infra-red spectra of 2-amino-methyl pyridines and amino-quinolines have been recorded in solutions at various concentrations. The N–H stretching frequencies have been assigned on the basis of the presence of intermolecular associations and primary amino group in these compounds. The bands in the region of 1600 cm.$^{-1}$ have been studied in considerable detail and the N–H deformation frequencies of monomer and associated molecules have been assigned. In all the amines studied, an absorption band appears in solutions of chloroform in the region of 2950 cm.$^{-1}$ which is not present in the spectra of pure amines or in solutions of carbon tetrachloride. The presence of this band has been explained as due to the associations between the free N-atom of the monomer amines and the H-atom of the chloroform.

VI. Acknowledgments

The authors thank Dr. M. R. Subbaram of Nutrition Research Laboratory, Hyderabad, for synthesising 2- and 4-amino-quinolines for this series of investigations.

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CONSTITUTION OF CAMPANULIN

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The isolation of the compound campanulin having the formula $C_{30}H_{50}O$ from the leaves of *R. campanulatum*, *R. falconeri*, and *R. barbatum* has been reported in earlier publications from these laboratories.[1-3] The properties of the compound have already been described by us in detail.[1] The fact that it does not undergo acetylation (later confirmed by absence of hydroxyl frequencies in the I.R. spectrum) and does not form derivatives characteristic of carbonyl compounds (later confirmed by absence of carbonyl frequency in the I.R. spectrum), but undergoes isomerization under the influence of mineral acids has also been reported by us.[2] Further reactions and transformations leading to the structure of the compound are described in the present paper.

Since campanulin gives the reactions characteristic of steroids and triterpenoids,[1] its I.R. spectrum indicates the presence of a *gem.*- dimethyl group (doublet at 1360 $cm.^{-1}$ and 1390 $cm.^{-1}$) and it occurs along with epifriedelanol[1] and friedelin[4] (which are definitely known to be triterpenoid compounds) it is also possibly a triterpenoid compound.

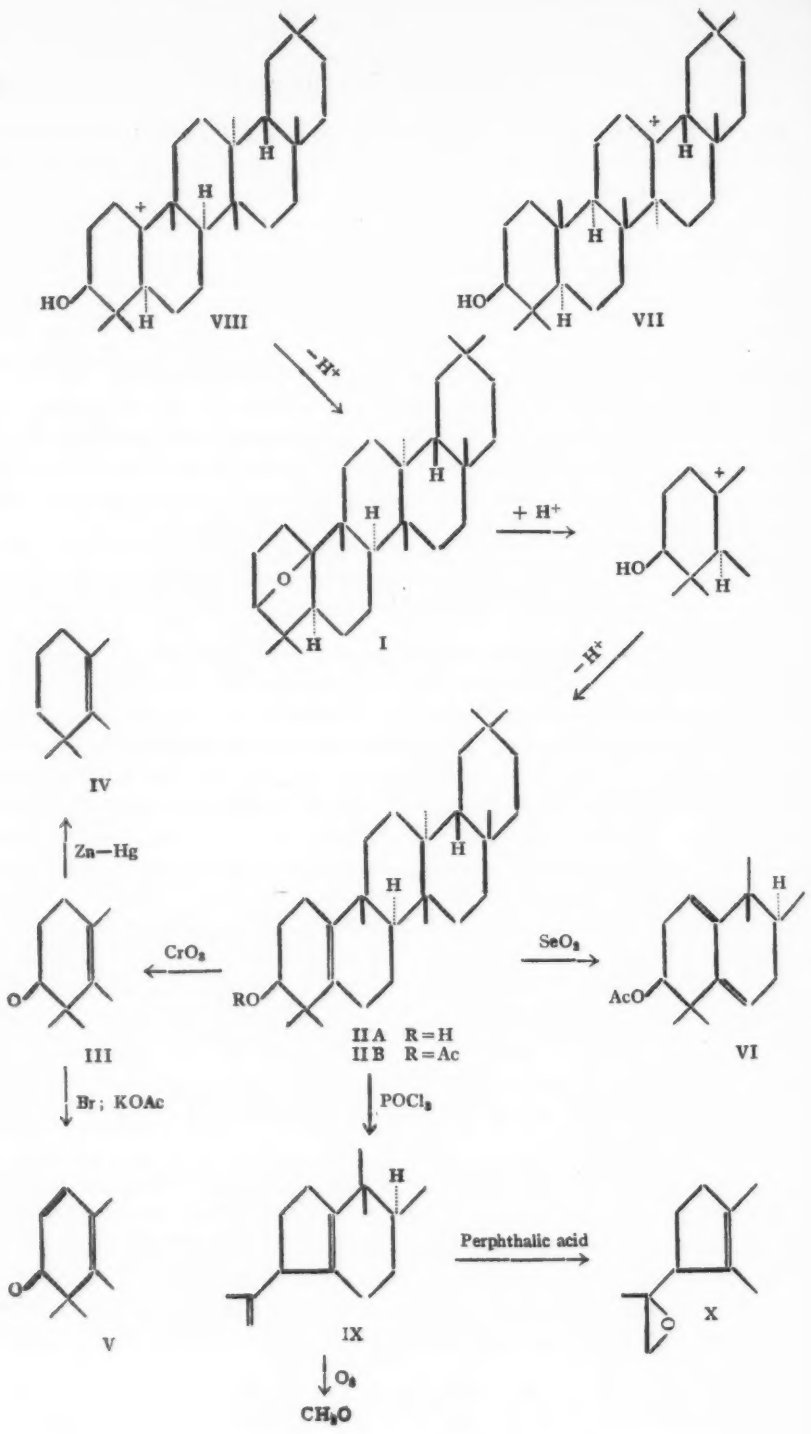
The compound has no unsaturation in it, since it does not give a colour with tetranitromethane in chloroform, does not react with perphthalic acid or undergo hydrogenation in presence of Adams PtO catalyst. The substance is free from methoxyl (micro-Zeisel) and was recovered after treatment with phosphorus oxychloride and pyridine (test for tertiary hydroxyl). These together with the earlier results regarding the nature of the oxygen function indicate that it is inert and possibly present as an oxide. In contrast to campanulin the product of isomerization with mineral acid underwent acetylation. Treatment of campanulin with *p*-toluene sulphonic acid-acetic anhydride, a reagent recommended by Ruzicka *et al.*[5] for splitting oxides, yielded a compound which was identical with the acetate of the isomerization product. These reactions show that campanulin should be a cyclic ether which opens out with mineral acids to give an alcohol and forms the alcohol acetate under the influence of *p*-toluene sulphonic acid-acetic anhydride. That this alcohol is a secondary alcohol was shown by its oxidation with

excess of CrO_3 to a ketone ($C_{30}H_{48}O$) (but not an acid) and by Clemmensen reduction of the ketone to a hydrocarbon, $C_{30}H_{50}$. The probable location of the carbonyl group at $C_{(3)}$ of the ketone was indicated by a pink colour in the Zimmermann reaction,[6] while the β-orientation of the hydroxyl at $C_{(3)}$ was indicated by the positive change in molecular rotation on acetylation ($\Delta\ [M]_D = +57°$).[7] The properties of the alcohol, its acetate, the ketone and the hydrocarbon corresponded respectively with those of alnus-5 (10)-en-3β-ol, its acetate, alnus-5 (10)-en-3-one and alnus-5 (10)-ene described by Beaton *et al.*[8] in almost all essential details. That the alcohol (II A), its acetate (II B) and the ketone (III) were really what they were suspected to be was confirmed by reaction of the alcohol acetate with SeO_2 to give alnusa-1 (10): 5-dien-3β-yl acetate (VI)[9] and by the ketone yielding alnusa-1: 5 (10)-dien-3-one (V) on treatment with bromine followed by potassium acetate.[8]

Final confirmation of the identity of the ketone was achieved by a direct mixed m.p. determination with a sample of alnus-5 (10)-en-3-one, kindly supplied by Dr. McLean from Professor Spring's collections.

The identity of the ketone (III) and of the alcohol (II A) having thus been established, the structure of the original compound campanulin follows from the following considerations. In contrast to the alcohol (isomerization product) which gives a positive reaction with tetranitromethane, campanulin does not give any colour with this reagent. This shows that the appearance of the (5: 10) double bond is a concomitant of the opening of the oxide ring to give the alcohol. Since one of the points of attachment of the oxygen is $C_{(3)}$, the other would be either at $C_{(5)}$ or $C_{(10)}$. Since the I.R. spectrum of campanulin shows a band at 9·1 μ which is considered to be characteristic of tetrahydrofurans, while a band at 10·2–10·3 μ characteristic of trimethylene oxides is missing in the spectrum (*see* Borrow and Searles[10]), the second point of attachment of the oxide seems to be $C_{(10)}$ and not $C_{(5)}$. This is perhaps to be expected from considerations of relative stability and also because the large majority of the known natural oxides have the oxygen atom present in a 5-atom ring. Hence campanulin can be represented by structure (I) in which the configuration of H at $C_{(5)}$ is assumed to be the same as in all well-known triterpenes.

In the course of their work on the constitution of alnusenone, Spring and coworkers[9] have suggested a scheme of biogenesis according to which β-amyrin, taraxerol, alnusenone and friedelin can all be derived from a common hypothetical precursor (VII) by changes involving the loss of a proton with or without being preceded by α shift of a methyl or hydrogen, each of which may take place only once or may be repeated twice or even more as necessary.


VIII
VII
$-H^+$
$+ H^+$
I
IV
Zn—Hg
CrO_3
SeO_3
III
IIA R=H
IIB R=Ac
VI
Br; KOAc
$POCl_3$
V
IX
Perphthalic acid
X
O_3
CH_2O

One of the intermediate stages in this scheme is represented by the structure (VIII) and it is quite conceivable that campanulin arises from this by loss of a proton from the C_3–OH.

It may be mentioned by the way that the compound (II A) underwent the retropinacolinic rearrangement on treatment with phosphorus oxychloride giving rise to (IX) which was characterized by its reaction with perphthalic acid to give an epoxide (X) and by the formation of formaldehyde on ozonolysis. The I.R. spectrum of (IX) included strong and sharp bands at 1634 cm.$^{-1}$ and 890 cm.$^{-1}$ which are characteristic of a vinylidene group, $\rangle C = CH_2$. This reaction has not been described in the literature so far and is therefore given here.

Experimental

For properties and analysis of campanulin *see* p. 100 of ref. 1. For the isomerization reaction yielding alcohol (II A) *see* p. 246 of ref. 2.* The acetate of the alcohol, prepared by heating with pyridine and acetic anhydride for 2 hours at 100°, crystallized from chloroform-acetone as colourless plates, m.p. 286–88°. $[\alpha]_D^{28°} = -17{\cdot}6° \pm 2°$ ($c = 0{\cdot}920$ in chloroform). Found: C, 81·7; H, 11·1. $C_{32}H_{52}O_2$ (II B) requires: C, 82·0; H, 11·2%.

Preparation of the acetate (II B) directly from campanulin.—A mixture of campanulin (0·1 g.), acetic anhydride (10 ml.) and *p*-toluene sulphonic acid (50 mg.) was heated at 115° for 45 minutes. It was cooled, ice-cold water (30 ml.) was added and left in the ice-chest overnight. The precipitate that separated was filtered, washed, dried and crystallized thrice from chloroform-acetone when shining colourless plates were obtained, m.p. 285–87° (80 mg.). $[\alpha]_D^{28°} = -14{\cdot}8° \pm 3°$ ($c = 0{\cdot}732$ in chloroform). Found: C, 82·3; H, 11·6. $C_{32}H_{52}O_2$ (II B) requires: C, 82·0; H, 11·2%. It gave a yellow colour with tetranitromethane in chloroform. Mixed m.p. with the sample prepared from (II A) was undepressed.

Preparation of ketone (III).—A solution of alcohol (II A) in benzene was treated with a 2% solution of chromic acid in acetic acid added dropwise with continuous shaking for a total period of 15 hours, an excess of the reagent being maintained throughout. Most of the solvents were removed under reduced pressure and the residual liquid was diluted with dilute sulphuric acid and extracted with ether. The ethereal extracts were washed with sodium carbonate solution and then with water, dried and the

* The molecular formula $C_{30}H_{48}O$ assigned to this alcohol in ref. 2 has to be revised to $C_{32}H_{52}O$ to conform to the formula of campanulin given in ref. 1.

solvent removed. Crystallization of the residue twice from chloroform-acetone yielded shining colourless prismatic plates, m.p. 250–51°. It gave a yellow colour with tetranitromethane in chloroform. A pink colour was obtained in the Zimmermann test. $[\alpha]_D^{28°} = -73{\cdot}4° \pm 2°$ ($c = 1{\cdot}062$ in chloroform). Found: C, 84·8; H, 12·0. $C_{30}H_{48}O$ (III) requires: C, 84·8; H, 11·4%. Mixed m.p. with an authentic sample of alnus-5 (10)-en-3-one (m.p. 251–52°) (from Professor Spring's collections) was undepressed.

The 2:4-dinitrophenylhydrazone, prepared in the usual way, crystallized from chloroform-alcohol as shining orange-red needles, m.p. 269–70°. Found: N, 10·1. $C_{36}H_{52}O_4N_4$ requires: N, 9·3%.

Preparation of hydrocarbon (IV).—To a boiling solution of ketone (III) (0·3 g.) in alcohol (200 ml.) and benzene (20 ml.) was added amalgamated zinc (65 g.), followed by conc. hydrochloric acid (2 ml.). Refluxing was continued for 36 hours with intermittent addition of further small quantities of acid and/or alcohol as and when required. The light yellow syrupy product which was obtained by working in the usual manner was subjected to vacuum sublimation (0·4 mm. pressure). Three fractions were obtained at 150–80°, 200–35° and 240–60° respectively. The first and the last fractions were amorphous. The middle fraction (90 mg.), on crystallization first from chloroform-alcohol and then from chloroform-acetone yielded thin colourless plates, m.p. 225–26° (23 mg.). $[\alpha]_D^{28°} = -35{\cdot}6° \pm 1°$ ($c = 0{\cdot}758$ in chloroform). Found: C, 86·8; H, 12·2. $C_{30}H_{50}$ (IV) requires: C, 87·7; H, 12·3%. It gave a yellow colour with tetranitromethane in chloroform.

Preparation of dienone (V) from (III).—This was prepared according to the method of Beaton *et al.*[8] using bromine in acetic acid followed by potassium acetate. The product which was impure was chromatographed over alumina. The petroleum ether-benzene (19:1 and 9:1) eluates yielded unconverted (III) (m.p. 249–52°). The petroleum ether-benzene (4:1 and 1:1) eluates yielded from chloroform-methanol shining yellow plates, m.p. 215–16°. Found: C, 84·7; H, 11·7. $C_{30}H_{46}O$ (V) requires: C, 85·3; H, 11·0%.

Selenium dioxide oxidation of acetate (II B) to (VI).—The oxidation was carried out as described in the literature.[9] The product which was purified by chromatography over alumina crystallized from chloroform-methanol as shining colourless plates, m.p. 206–07°. $[\alpha]_D^{29°} = +118{\cdot}7° \pm 2°$ ($c = 1{\cdot}365$ in chloroform). Found: C, 82·0; H, 11·6. $C_{32}H_{50}O_2$ (VI) requires: C, 82·3; H, 10·8%. It gave a deep orange colour with tetranitromethane.

Preparation of (IX).—A solution of the alcohol (II A) (1 g.) in pyridine (400 ml.) was treated with phosphorus oxychloride (55 ml.) drop by drop with stirring. The reaction mixture was left at room temperature for 16 hours and then heated on a steam-bath for 30 minutes. The resulting dark brown solution was cooled and poured slowly on crushed ice. The yellow aqueous solution was extracted with petroleum ether (8 × 100 ml.), the extract was washed with water, then with 2 N hydrochloric acid and finally with water till neutral. It was dried and filtered through a column of alumina (3 g.). Evaporation of the filtrate gave a reddish yellow residue, which on crystallization thrice from chloroform-acetone yielded shining colourless plates, m.p. 195–97° (0·48 g.). $[\alpha]_D^{27} = -53{\cdot}0° \pm 1°$ ($c = 1{\cdot}464$ in chloroform). Found: C, 87·9; H, 12·5. $C_{30}H_{48}$ (IX) requires: C, 88·1; H, 11·8%. It gave a deep yellow colour with tetranitromethane in chloroform.

Preparation of epoxide (X).—A solution of (IX) (50 mg.) in chloroform (5 ml.) was treated at − 10° with excess of a solution of monoperphthalic acid in chloroform. The mixture was left in the ice-chest for two days and worked up in the usual manner. The product crystallized from chloroform-acetone as colourless nodules, m.p. 209–11°. Found: C, 84·2; H, 11·9, $C_{30}H_{48}O$ (X) requires: C, 84·8; H, 11·4%.

Ozonolysis of (IX)—detection of formaldehyde.—A solution of (IX) (0·4 g.) in dry chloroform (30 ml.) was treated at − 10° with ozonised oxygen (1·5% O_3 content) (*ca.* 100 ml. per minute) for 25 minutes. After attaining room temperature, the solution was treated with acetic acid (3 ml.) and portionwise with zinc dust (0·6 g.) over 30 minutes with stirring. After 1 hour's stirring, the solution was filtered and the filtrate washed with water (3 × 15 ml.). The aqueous washings were combined, adjusted to pH 7·0 by the addition of solid sodium bicarbonate when a colourless precipitate separated, which was filtered. The clear, colourless filtrate gave with saturated aqueous solution of dimedone a colourless precipitate which crystallized from alcohol as colourless needles (10 mg.), m.p. 192–93°, undepressed by admixture with authentic formaldehyde-dimedone compound.

Summary

Experiments leading to the establishment of the constitution of campanulin are described and discussed.

Acknowledgments

The authors express their gratitude to Professor Spring and Dr. J. McLean of Royal College of Science and Technology, Glasgow, for kindly supplying

the reference sample of alnus-5 (10)-en-3-one and Professor T. R. Govindachari of the Presidency College, Madras, for taking the infra-red spectra of the several compounds discussed in this paper. We thank Mr. R. V. Krishna Rao for microanalyses.

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EPILOGUE

The work described in this article including the experiments, observations, interpretations and conclusions and also biogenetic relationships, formed part of a thesis submitted by one of the authors (K. S. M.) for the D.Sc. degree of the Andhra University, Waltair, in August 1960. The thesis was approved in December 1960 and a copy of the same was deposited in the INSDOC Library at New Delhi in the same month. It has become necessary to state these facts because in the number of the *J. Chem. Soc.* (Feb. 1961) which has been received in our library a few days back, there is an article from the Hong-Kong University (H. R. Arthur and Miss W. H. Hui, p. 551) which deals obviously with the same substance as our own, though the experiments that they have described do not tally with our own. In their earlier publication (H. R. Arthur, C. M. Lee and C. N. Ma, *J. Chem. Soc.*, 1956, 1461) describing the isolation of their compound, they reported the specific rotation as $-80°$, but have completely reversed the sign (to

+ 74·8°) in their present paper. Since our own substance had a specific rotation of + 75·2° we were misled into concluding that we were not dealing with the same substance as theirs and into believing that there was no special urgency about the publication of our own findings, though our work was completed long before August 1960 (the date of submission of the thesis mentioned above).

DECAY-TIME OF SCINTILLATIONS IN CsI (Tl) CRYSTAL

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Received August 1, 1961

Introduction

It is known that crystals of alkali halides activated with thallium are efficient scintillators. Because of their simplicity of crystalline structure, confinement of luminescence emission to thallium centres, and the possibility of using photomultiplier tubes to study the characteristics of their light emission, a detailed study of these crystals when excited by nuclear radiations is desirable.

It was reported earlier (Lagu and Thosar, 1961) that a single crystal of CsI (Tl) emits two prominent bands in the visible region when excited by γ-rays or ultra-violet. One is a band in the blue, and the other is a doublet band in the yellow. The emission spectra, both under γ-rays and ultra-violet excitations, show maxima centred around the same wavelengths, indicating that the luminescent centre responsible for emission in the two cases is the same. Assuming that thallium ion is the centre of luminescence, these emission bands are the result of de-excitation of the excited levels of this localised centre. In such a case, it is possible to have different transition probabilities for the processes giving the two emission bands. Measurement of the decay times of luminescence in these individual bands is necessary to obtain information about the transition probabilities.

Experimental Procedure

A study of decay times of scintillations of CsI (Tl) was made under excitation by γ-rays of energy 1·3 Mev. from a Co^{60} source and under α-particles from a Polonium source (S in Fig. 1). Suitable filters F were interposed between the crystal C and the photomultiplier to isolate the two emission regions, blue and yellow. The transmission characteristics of the filters in relation to the emission bands are shown in Fig. 2.

The method of measurement of decay time consists in investigating the shape of the voltage pulse at the anode of a photomultiplier tube (6810 A) which views the scintillation light pulses from the crystal CsI (Tl) (Fig. 1).

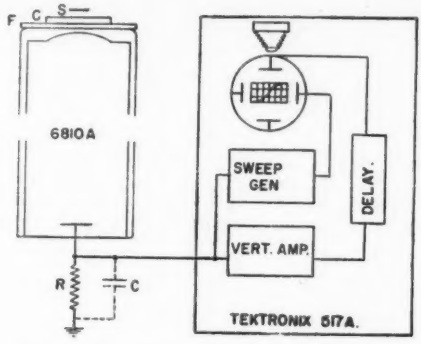

FIG. 1. Schematic diagram of experimental arrangement.

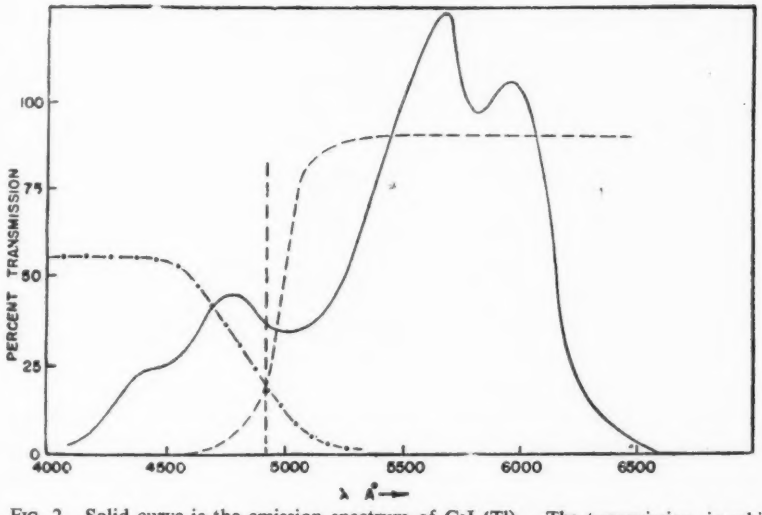

FIG. 2. Solid curve is the emission spectrum of CsI (Tl). The transmission, in arbitrary units, for the blue (—·—·) and yellow (– – – –) filters is also shown.

If the light pulse follows an exponential decay the height of the voltage pulse V at any instant of time t from the start of the pulse is given by

$$V(t) = \frac{V_0}{\tau - RC} \{e^{-t/\tau} - e^{-t/RC}\}$$

where τ is the decay time of the light pulse, RC is the effective time constant of the anode load of the photomultiplier tube and V_0 is the maximum height

of the pulse. V_0 depends on the total number of photons emitted by the crystal due to absorption of a γ-ray or an α-particle.

(i) When RC is made much larger compared to τ, the shape of the voltage pulse is an inverted exponential whose rise time corresponds to the decay time of the light pulse. If there are two components of decay, the shorter component would be integrated first. If the long component is about ten times larger than the short component, the rise part of the voltage pulse corresponds to the short component decay time. In the present experiment the short component of decay was measured by a method of adjusted magnification, which is explained below.

A standard exponential is drawn on a sheet of graph paper. The photographic negative of the oscilloscope trace of the pulse is put in an enlarger. The magnification of the projected image is adjusted such that with the base line of the drawn exponential coincident with the line at maximum height of the pulse the image of the pulse and the standard curve coincide with each other (Fig. 3). When this happens, it is obvious that $V_0\, e^{-x} = V_0\, e^{-t/\tau}$. Then, $x.\tau = t$, or $\tau = t$ for $x = 1$. So, the time t on

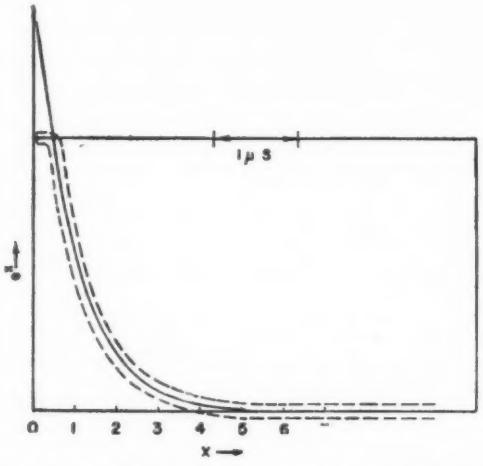

FIG. 3. Method of adjusted magnification. $x = 1$ on standard exponential (solid curve) corresponds to $0{\cdot}5\,\mu$ sec. on the scale of the projected pulse image (dotted curves) when fitted. The pulse, with base line at the top, is due to alpha-rays, with yellow filter and RC = $10\,\mu$ sec.

the trace image, corresponding to $x = 1$ on the graph sheet, equals the decay time τ. In this way, analysis becomes easy, and the results are comparable

in accuracy to the method of least squares, since every part of interest on the pulse image is used for comparison with the standard exponential.

(ii) In the non-integrating method, RC is made much smaller than τ and then the decay of the voltage pulse corresponds to the decay of the light pulse. However, because the smoothing action of the integrated pulse method is now negligible, the pulse looks jagged. This effect is more pronounced if the number of photoelectrons ejected by the photocathode becomes small, as was the case when filters had to be used between crystal and photomultiplier. If RC is of the order of τ/n where n is the total number of photoelectrons from cathode per pulse, then pulses due to single electrons leaving cathode can be seen. These will be called elementary pulses hereafter. The elementary pulses can be counted provided there is no optical integration due to finite width of the oscilloscope beam trace. The amount of optical overlap depends on the sweep speed. At high speeds, the time interval corresponding to the size of the spot is small and the individual pulses are well separated. But only a small portion of the entire pulse is seen since the time for the visible length of the trace is small at higher sweep speeds. In a compromise situation, there will be some optical integration at the beginning of the pulses, but counting of individual elementary pulses over a reasonable length of the pulse can be made. A least squares fit to the numbers of photoelectrons from cathode counted in this manner, for successive equal time intervals, gives a value of the long component of the decay time. This method had to be used in the present experiment, where very low light level measurements were encountered. When only a few photons are emitted per pulse, the term decay time loses its significance.

At the limit of low light level measuremens of decay times, there is a problem worth mentioning. When RC becomes so small that electronic integration is absent even for the first few photoelectrons, then the trace-initiating trigger level for the oscilloscope has to be small enough, to be operated by the first photoelectron. In this case, even thermal electrons released from the photocathode can trigger the scope trace. To reduce the number of such unwanted trace triggers, which cause an unwelcome fogging of the negative, the photocathode may have to be cooled. Besides, the method obviously fails when the number of elementary pulses counted per the chosen time interval becomes comparable to the number of thermal electrons from the cathode.

The short component of decay was investigated by the first method of adjusted magnification described above, with $RC = 10\,\mu s$. The long

components of decay were measured by the second method, with an estimated RC = 10 *ns*.

RESULTS AND DISCUSSION

The results obtained for the decay time for the short and long components of decay in CsI (Tl) by the two methods described above, are summarised in Table I. This gives the values of τ_1 and τ_2 for the two

TABLE I

Excitant	τ_1 in μ sec.		τ_2 in μ sec.	
	Blue	Yellow	Blue	Yellow
Po–α ..	$0{\cdot}51 \pm {\cdot}02$	$0{\cdot}49 \pm {\cdot}02$	$12{\cdot}1 \pm 2{\cdot}0$	$9{\cdot}5 \pm 2{\cdot}0$
Co–γ ..	$0{\cdot}89 \pm {\cdot}06$	$0{\cdot}99 \pm {\cdot}06$	$7{\cdot}6 \pm 2{\cdot}0$	$9{\cdot}8 \pm 2{\cdot}0$

emission bands, blue and yellow excited with Polonium α-rays and Cobalt-60 γ-rays. About 15 to 20 pulse traces of each kind were examined to arrive at the average values. The limits of probable error are indicated. It may be seen that within the limits of experimental error there is no change in the decay time for the two emission bands, blue and yellow. This is true for both short- and long-lived decay components and whatever the exciting radiation. In the case of short-lived decay component τ_1, in both the blue and yellow bands, the decay time is significantly smaller for α-ray excitation than for γ-rays. In the case of the long-lived component of decay, the variation in decay time, if any, with the nature of exciting radiation, is within the limits of experimental error and is not significant.

There is a marked decrease in the decay time of the short-lived component when the crystal is excited by α-particles instead of by γ-rays. A similar trend was observed by Storey, Jack and Ward (1958) who studied the decay time for a thin crystal of CsI (Tl), using α-particles, protons and electrons as excitant. The decrease in τ with increasing ionization density reported by them is in agreement with the above results. A change in decay time of scintillations with the nature of exciting radiation for NaI (Tl) crystal was reported earlier (Thosar and others, 1959).

SUMMARY

Decay times of scintillations excited in a CsI (Tl) crystal by α-particles and γ-rays have been studied for the two regions of the emission spectrum,

blue and yellow. Voltage pulses from a photo-multiplier tube, viewing the crystal, as seen on a high-speed oscilloscope have been photographed and investigated. There are two decay components, short- and long-lived. In the case of the long-lived component ($\tau = 10\,\mu$ sec.) there is no significant variation in decay time with the nature of excitant or the type of emission band. In the case of the short-lived component there is no variation with the type of emission band but there is a marked decrease in the decay time for α-particle excitation ($\tau = 0{\cdot}5\,\mu$ sec.) compared to that for γ-rays ($\tau = 0{\cdot}9\,\mu$ sec.).

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RAMAN AND INFRA-RED SPECTRA OF AMINES

Toluidines and *para*-amino-acetophenone

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I. Introduction

The Raman spectra of toluidines ($CH_3.Ph.NH_2$) have been recorded by Herz *et al.*[1] and Kohlrausch.[2] Kohlrausch[3] assigned the stretching and bending frequencies of the methyl group of these amines. Califano *et al.*[4] recorded the infra-red spectra of *para*- and *meta*-toluidines. The earlier workers do not appear to have recorded the N–H vibrational frequencies in the Raman spectra of toluidines. The authors recorded the Raman and infra-red spectra of toluidines and *para*-amino-acetophenone ($Ph.NH_2.CH_3C=0$) in order to (*a*) assign the N–H stretching and deformation frequencies, (*b*) study the effect of solvent on the N–H vibrational frequencies, and (*c*) investigate the dielectric effects by the application of Bellamy's formula.[5]

II. Experimental

A Fuess glass spectrograph with a dispersion of 19 $cm.^{-1}$ per mm. in the region of 4358 Å was used along with the Hilger Raman Source Unit to record the Raman spectra. λ 4358 was the exciting radiation. The *meta*- and *ortho*-toluidines, when distilled under reduced pressure, are colourless. But they get easily coloured when exposed to mercury light. While recording the Raman spectra, the liquid in the Raman tube was therefore replaced by fresh liquid every five minutes. As *p*-amino-acetophenone is a solid, its Raman spectrum was recorded in solution of chloroform.

A Perkin Elmer Model 21 infra-red spectrophotometer, with NaCl optics, was used to record the infra-red spectra. The spectra of liquids were recorded by pressing a drop of each liquid between two NaCl plates so as to form a microfilm of unknown thickness and the spectra of solids were obtained by mull technique. For recording the infra-red spectra of solutions, matching cells of 0·1 mm. thickness were used.

III. Results

The experimental procedure mentioned above for recording the Raman spectra has enabled the authors to record a number of faint lines in the spectra of *ortho-* and *meta*-toluidines which would otherwise have been missed due to colouration of the liquid and the consequent absorption of incident light. The Raman and infra-red frequencies of the amines, as recorded by the authors, are given in Table I.

In the Raman spectra of *ortho-* and *meta*-toluidines, the authors could record two lines in the region of 3450 and 3370 cm.$^{-1}$ The line at lower frequency has a banded structure and the one at higher frequency is sharp and faint. These Raman frequencies are in good agreement with the corresponding frequencies in the infra-red spectra.

IV. Discussion

The N–H stretching frequencies of the amines and in various solvents are given in Table II.

The authors could record the N–H asymmetric and symmetric stretching frequencies in the Raman spectra of *ortho-* and *meta*-toluidines and these frequencies are in fair agreement with those of the N–H stretching absorption bands in the infra-red spectra. The N–H stretching frequencies of the amines in solutions of CCl_4 or $CHCl_3$ are higher than those of the pure amines. The N–H stretching frequencies of *p*-amino-acetophenone in chloroform are higher than those of the corresponding bands of toluidines in the same solvent. Flett[6] studied a number of substituted anilines and attributed the high frequencies in the region of 3535 and 3436 cm.$^{-1}$ in case of *p*-nitro aniline as due to the electron attracting ability of the nitrogroup in the *para* position. The higher N–H stretching frequencies of *p*-amino-acetophenone in solution of chloroform may from similar reasoning be due to the electron withdrawing capacity of the acetyl group ($CH_3C = O$) in *para* position.

N–H Deformation and Ring Frequencies.—The N–H deformation and ring frequencies, recorded in the Raman and infra-red spectra of the amines, are given in Table II. The infra-red spectrum of *meta*-toluidine has a strong and wide absorption band extending from 1594 to 1628 cm.$^{-1}$ and in the Raman spectrum also, it has a banded structure extending from 1585 to 1612 cm.$^{-1}$ The band in the infra-red could be resolved into two peaks at 1628 and 1594 cm.$^{-1}$, in solution of dioxane and they are at 1623 and 1594 cm.$^{-1}$ in carbon tetrachloride. But the Raman spectrum of *ortho*-toluidine

TABLE I

Raman and infra-red spectra of amines (cm.$^{-1}$)

o-toluidine		*m*-toluidine		*p*-amino-acetophenone in chloroform	
Raman	Infra-red	Raman	Infra-red	Raman	Infra-red
185 (3)	..	217 (4)	..	..	..
263 (3)	..	238 (4)	..	..	..
317 (0)	..	294 (4)	..	..	..
509 (3)	..	519 (3)	..	..	..
579 (3)	..	543 (3)	..	..	..
682 (0)	714 (w)	679 (0)	684 (m)	..	..
739 (7)	753 (s br)	736 (8)	..	..	..
..	..	776 (1)	777 (s br)	..	..
..	..	..	..	..	832 (m)
841 (2)	845 (m)	849 (0)	856 (m)	843 (3)	..
..	..	893 (0)	870 (m)	..	..
923 (0)	926 (m)	935 (1)	926 (m)	957 (2)	957 (m)
980 (2)	986 (m)	995 (9)	998 (m)	985 (5)	1020 (w)
1029 (5)	1035 (m)	..	1037 (w)	..	..
1081 (0)	1064 (w)	1077 (0)	1078 (w)	1075 (5)	1073 (w)
1145 (3)	1142 (m)	1157 (2)	1170 (s)	..	1130 (w)
1198 (4)	1199 (vw)	..	..	1179 (3)	1176 (s)
1265 (5)	1270 (vs)	1295 (6)	1292 (s)	1279 (1)	1276 (s)
..	1302 (s)	..	1311 (m)	..	1300 (s)
1309 (1)	1316 (w)	..	..	..	..
1376 (3)	1379 (m)	1377 (4)	1376 (w)	..	1361 (s)
1436 (0)	1444 (m)	..	1451 (w)	1433 (2)	1439 (w)
1487 (0)	1493 (s)	1480 (0)	1493 (s)	..	..
..	1503 (s)	..	..	..	..
..	1510 (w)	..	1511 (w)	1513 (1)	1515 (m)
1582 (3)	1585 (m)	1585	1594	1568 (3)	1567 (m)
1601 (4)	1610 (vs)	to (4)	to (vs)	1599 (6)	1597 (s)
1615 (3)	1628 (vs)	1612	1628	1623 (2)	1623 (s)
..	..	..	..	1664 (4)	1669 (s)
2871 (3)	2865 (w)	2869 (3)	2880 (w)	..	..
2919 (3)	2915 (ms)	2915 (3)	2920 (w)	..	..
2989 (1)	3025 (ms)	3011 (1)	3025 (ms)	..	..
..	3225 (w)	..	3225 (w)	..	3225 (w)
3374 (4)	3365 (s)	3370 (4)	3355 (s)	..	3430 (s)
3451 (1)	3450 (m)	3455 (1)	3435 (m)	..	3520 (m)

V.S=Very strong, *S*=(*S*, *br*) = strong and broad, *m*=medium, *w*= weak, *vw*=Very weak.

TABLE II

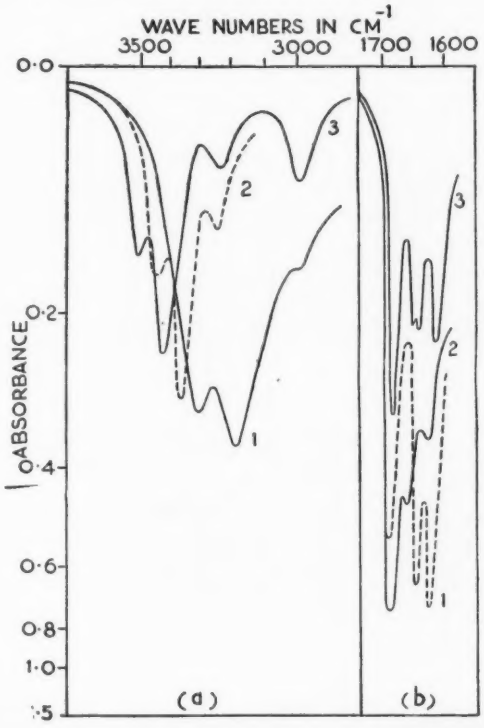
N–H stretching and bending frequencies of the amines and in various solvents

Solvent	Nature of the band	*p*-Toluidine		*m*-Toluidine		*o*-Toluidine		*p*-Amino-acetophenone
		Infra-red	Raman	Infra-red	Raman	Infra-red	Raman	Infra-red
Pure amine ..	N–H stretch	3455, 3365	3455, 3370	3435, 3355	3451, 3374	3450, 3365	..	3415, 3335
..	N–H deform	1628	1585–1612	1594–1628	1615	1628	..	1640
CCl_4 or $CHCl_3$ ..	N–H stretch	3490, 3400	..	3490, 3400	..	3490, 3405	..	3520, 3430
..	N–H deform	1621	..	1623	..	1622	1623	1623
Pyridine ..	N–H stretch	3335, 3225	..	3335, 3220	..	3335, 3225	..	3315, 3175
..	N–H deform	1642 (w)	1621	1642	1625	1642	1637	1645
Dioxane ..	N–H stretch	3455, 3370	..	3455, 3370	..	3460, 3380	..	3450, 3365
..	N–H deform	1628	..	1623	..	1628	..	1634

has two distinct lines at 1615 and 1601 cm.$^{-1}$ and the line at higher frequency has banded structure. The corresponding infra-red absorptions are two well-defined bands at 1628 and 1610 cm.$^{-1}$ These frequencies in the infra-red have same values in solution of dioxane, but in solutions of CCl_4 the absorption at 1628 cm.$^{-1}$ shifts to 1622 cm.$^{-1}$ and the one at 1610 cm.$^{-1}$ to 1616 cm.$^{-1}$ with the result that the lower frequency appeared as a poorly resolved shoulder. The infra-red spectrum of *p*-toluidine has a single strong absorption at band 1628 cm.$^{-1}$ and its frequency is the same in solution of dioxane. But in solution of CCl_4, the band shifts to 1621 cm.$^{-1}$ and in pyridine it is a strong absorption band at 1621 cm.$^{-1}$ together with a weak peak at 1642 cm.$^{-1}$ From these results the authors assign the absorption bands at 1622 and 1623 cm.$^{-1}$ of *ortho*- and *meta*-toluidines in CCl_4 or the Raman line at 1615 cm.$^{-}$ of *o*-toluidine to N–H inplane deformation vibrations and the peaks at 1610 and 1594 cm.$^{-1}$ of the same amines in infra-red or the Raman frequency at 1601 cm.$^{-1}$ of *o*-toluidine are assigned to the ring vibrations. The Raman line in *m*-toluidine extending from 1585 to 1612 cm.$^{-1}$ may be due to the overlapping of the lines arising out of the N–H inplane deformation and ring vibrations. Similarly the single strong absorption of *p*-toluidine at 1628 cm.$^{-1}$ or of it in CCl_4 at 1621 cm.$^{-1}$ may not be entirely due to N–H inplane deformation vibration. The N–H deformation band of *p*-amino-acetophenone is at 1640 cm.$^{-1}$ in the infra-red and it shifts to 1623 cm.$^{-1}$ in solution chloroform. The corresponding Raman frequency in solutions of chloroform is a sharp line at 1623 cm.$^{-1}$ These assignments are substantiated by the fact that the frequencies assigned to N–H inplane deformation vibrations of these amines are not present in the infra-red spectrum of toluene recorded by the authors or in the Raman spectrum of acetophenone.[7] In addition, the N–H inplane deformation frequencies could be recorded in the same region in heterocyclic amines.[8, 9]

Solvent Effect.—The N–H stretching and deformation frequencies of the amines in solutions of pyridine and dioxane are given in Table II, and the corresponding infra-red absorption bands of *p*-amino-acetophenone are given in Text-Fig. 1. The shifts in the Raman N–H deformation frequencies of the amines in solutions of pyridine are shown in Plate VI. In solutions of pyridine, the N–H stretching frequencies shift towards lower values to the extent of 150 cm.$^{-1}$ and N–H inplane deformation frequencies increase by about 20 cm.$^{-1}$ compared to the corresponding frequencies in solution of CCl_4. In addition, the N–H deformation frequencies become weaker in solutions of pyridine. The N–H deformation lines in the Raman spectra show clear shifts towards higher frequency in solutions of pyridine as shown

in Plate VI. These results indicate that in solutions of pyridine, the amines form strong hydrogen bonds of N–H ··· N type.



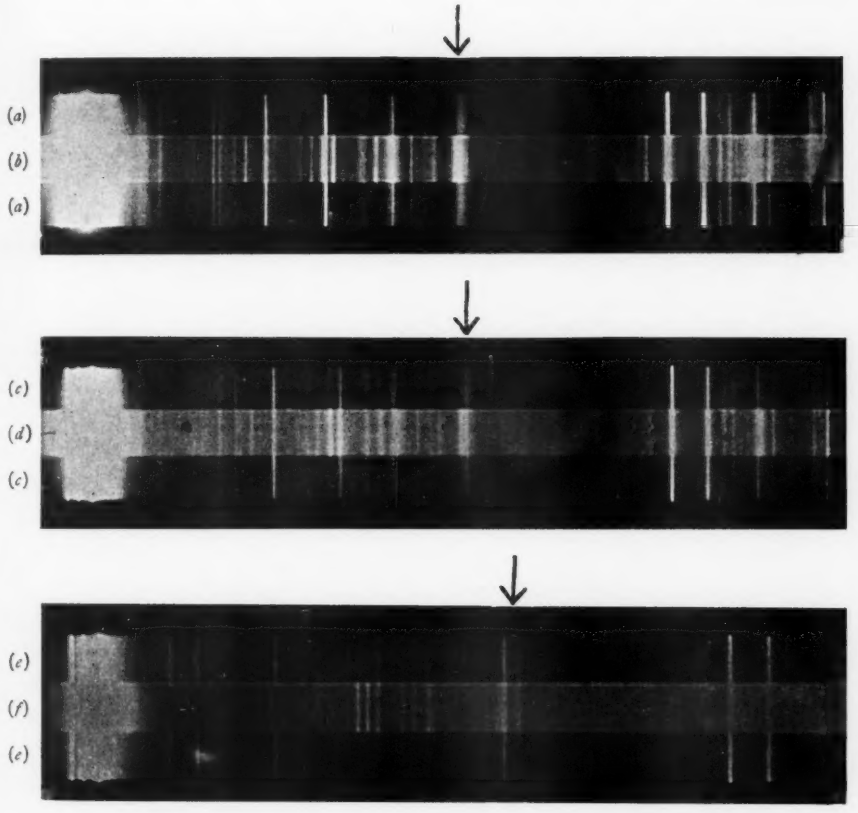
TEXT-FIG. 1. Infra-red spectrum of *p*-amino-acetophenone. (*a*) N-H and C-H stretching frequencies; (1) In pyridine (0·42 mol. conc.), (2) in dioxane (0·22 mol. conc.), (3) in chloroform (0·36 mol. conc.); (*b*) C = O stretch, N-H deformation and Ring frequencies (1) in chloroform (0·25 mol. conc.), (2) in pyridine (0·42 mol. conc.), (3) in dioxane (0·074 mol. conc.).

Dielectric Effects.—Bellamy *et al.*[5] have proposed that the N–H asymmetric and symmetric stretching frequencies of aromatic primary amines are governed by the relation $\nu_s = 345{\cdot}5 + 0{\cdot}875\ \nu_{as}$. These authors mention that this relation does not hold good in cases where only one of the N–H links of the amines is in the bonded condition. The N–H stretching frequencies of toluidines shift to the extent of 50 cm.$^{-1}$ in solutions of CCl_4 or $CHCl_3$. In order to arrive at a conclusion whether this shift is due to associations through N–H ··· N bonds or due to dielectric effects, the authors inserted the asymmetric stretching frequencies of the amines in the above relation and calculated the corresponding symmetric stretching

TABLE III

Calculated and observed N-H stretching frequencies of the amines and in various solvents

Solvent	*p*-Toluidine			*m*-Toluidine			*o*-Toluidine			*p*-Amino-acetophenone		
	Observed		Calculated	Observed		Calculated	Observed		Calculated	Observed		Calculated
	ν_{as}	ν_s	ν_s	ν_{as}	ν_s	ν_s	ν_{as}	ν_s	ν_s	ν_{as}	ν_s	ν_s
Pure amine ..	3455	3365	3369	3435	3355	3351	3450	3365	3364	3415	3335	3334
Carbon tetrachloride or chloroform	3490	3400	3400	3490	3400	3400	3490	3405	3400	3520	3430	3426
Pyridine ..	3335	3225	3263	3335	3200	3263	3335	3225	3263	3315	3175	3246
Dioxane ..	3455	3270	3369	3455	3370	3369	3460	3380	3374	3450	3365	3364



Raman spectra of:

(*a*) Pure *Meta*-Toluidine.
(*b*) *Meta*-Toluidine with Pyridine. Ratio 1:2 by Vol.
(*c*) Pure *Ortho*-Toluidine.
(*d*) *Ortho*-Toluidine with Pyridine. Ratio 1:2 by Vol.
(*e*) *Para*-Amino Acetophenone with Chloroform (0·66 Mol. conc.).
(*f*) *Para*-Amino Acetophenone with Pyridine (0·57 Mol. conc.).
(Arrow mark indicates the line that has shifted).

frequencies. The recorded and calculated values of the N–H stretching frequencies of the amines and in various solvents are given in Table III. It is seen from these observations that the relation proposed by Bellamy *et al.* is obeyed in case of the N–H stretching frequencies of the amines and in solutions of CCl_4 and dioxane. The N–H $\cdots$ N or the N–H $\cdots$ O bonding in pure amines or in solution of dioxane would lead to non-equivalent N–H links, whereas the dielectric effects would influence both the N–H links equally, these results indicate that the association through hydrogen bonds is unlikely in these cases. On the other hand, the empirical relation of Bellamy *et al.*[5] is not obeyed in case of the N–H stretching frequencies of the amines in solutions of pyridine. The average deviation between the observed and calculated symmetric stretching frequencies is of the order of 50 $cm.^{-1}$ This result indicates that only one of the N–H links of the amines is bonded in solutions of pyridine and the asymmetry thus introduced leads to the breakdown of the above relation. It would appear that it is not sterically possible for two molecules of pyridine to bond to the same NH_2 group of the amines.

V. Summary

The Raman and infra-red spectra of toluidines and *para*-amino-acetophenone have been recorded and the N–H stretching and bending frequencies of these amines have been assigned. The effect of solvent on the N–H stretching and deformation frequencies of the amines is investigated and their variation in solutions of pyridine is accounted for as due to the N–H $\cdots$ N bonding. The empirical formula proposed by Bellamy for the N–H stretching frequencies of amines has been used for the amines under investigation. The formula is obeyed for the N–H stretching frequencies of amines and in solutions of carbon tetrachloride, chloroform or dioxane, but it breaks down for the same frequencies in pyridine. These results are explained.

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